

# PATENT ABSTRACTS OF JAPAN

(11)Publication number : 11-327139

(43)Date of publication of application : 26.11.1999

(51)Int.Cl.

G03F 7/038  
G03F 7/038  
C08F290/12  
C09D 4/06  
C09D201/02

(21)Application number : 10-134122

(71)Applicant : NIPPON KAYAKU CO LTD

(22)Date of filing : 18.05.1998

(72)Inventor : YOKOSHIMA MINORU

OKUBO TETSUO

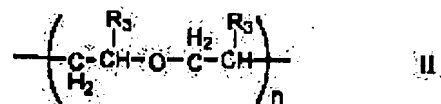
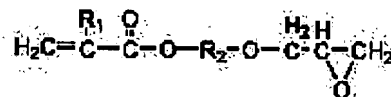
SASAHARA KAZUNORI

## (54) RESIN COMPOSITION AND ITS HARDENED MATERIAL

### (57)Abstract:

**PROBLEM TO BE SOLVED:** To provide a resin composition being capable of development by use of alkali aqueous solution, having heat resistance and resistance against solvent, and suitable for a permanent resist by making a carboxyl group in a polymer containing at least one carboxyl group contain a compound and a diluent to which a specified compound is added.

**SOLUTION:** A carboxyl group in a polymer containing at least one carboxyl group contains a compound or a diluent to which a compound represented by a formula I is added. Acryl resin is favorably used as the polymer. In the formula I, R1 is hydrogen atom or methyl group, R2 is alkylene, cyclohexane-1, 4-dimethylene or binding chain represented by a formula II, having 2-4 carbon atoms, R3 is hydrogen atom, methyl or ethyl group and (n) is a number of 1-5. It is desirably that the compound represented by the formula I is 4- glycidyletherbuthylacrylate.



## LEGAL STATUS

[Date of request for examination]

[Date of sending the examiner's decision of rejection]

[Kind of final disposal of application other than the examiner's decision of rejection or application converted registration]

[Date of final disposal for application]

[Patent number]

[Date of registration]

[Number of appeal against examiner's decision of rejection]

[Date of requesting appeal against examiner's decision of rejection]

[Date of extinction of right]

**\* NOTICES \***

JPO and INPIT are not responsible for any damages caused by the use of this translation.

- 1.This document has been translated by computer. So the translation may not reflect the original precisely.
- 2.\*\*\*\* shows the word which can not be translated.
- 3.In the drawings, any words are not translated.

---

**DETAILED DESCRIPTION**

---

[Detailed Description of the Invention]

[0001]

[Field of the Invention] This invention relates to a resin constituent especially a resin constituent useful as an object for the permanent resists of a printed wired board, and its hardened material.

[0002]

[Description of the Prior Art] Although the printed wired board is conventionally manufactured using copper clad laminate by the subtractive process which removes an unnecessary copper foil part by etching in a circuit, it is the present condition that it has faults, like that this subtractive process is difficult to form a fine pattern and a high density patchboard and minor diameter SURUHORU, and the Bahia hall cannot carry out to homogeneity in electroplating, and it is impossible to be unable to respond to the densification of electronic equipment.

[0003] On the other hand, the fully-additive process which forms an adhesives layer in the laminate which consists of an insulating base material recently, and forms a circuit and SURUHORU there by electroless deposition attracts attention. by this approach, conductor pattern precision is determined only in the imprint precision of a plating resist -- having -- moreover, a conductor -- since a part is formed only by electroless deposition, also in the substrate which has high aspect ratio SURUHORU, it is possible to perform uniform high SURUHORU plating of throwing power. Although it is the additive process it has been supposed until now that it is suitable for a general noncommercial use of an additive process, it is beginning to use as industrial use, high density, and a Kota layer substrate manufacture process.

[0004]

[Problem(s) to be Solved by the Invention] Generally, with the additive process for the radical version manufacture of a noncommercial way, although the plating resist pattern is imprinted by screen printing, in order to manufacture the printed wired board which has high density wiring, it is necessary to form a plating resist pattern by photoengraving process, i.e., to adopt the photograph additive process using a photoresist. The following properties other than a property of photoresist original like development nature are required of the photoresist suitable for a photograph additive process sensibility and whenever [ development ]. Since the pharmaceutical preparation used at a development process is limited to a 1,1,1-trichloroethane system organic solvent or an alkali water solution, Are equal to the electroless deposition performed for a long time under that development is possible at either, an elevated temperature, and high alkaline conditions, It has the solder resist property which was excellent as a permanent resist after plating processing, It is having the thermal resistance which also bears the temperature around 260 degrees C in a soldering process, having the solvent resistance over the organic solvent which washes the flux used at the time of soldering, not reducing the thermal dependability of the whole substrate further, even if a laminating's is carried out, etc. Although the usable photoresist is also marketed by current and this additive process, it cannot be said that that engine performance is still enough.

[0005] The resist formation with a sufficient pattern precision the place made into the purpose of this

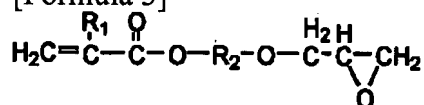
invention with a photographic method Therefore, an alkali water solution Are possible in the development (using [ for example, ] the sodium-carbonate water solution, the KOH water solution, the diethanolamine water solution), etc. The thermal resistance which fully bears the non-electrolytic copper plating liquid of a fully-additive process, and also bears the temperature around 260 degrees C of a soldering process, And it is in offering the resin constituent suitable for the permanent resist used without having the solvent resistance over the organic solvent which washes the flux used at the time of soldering, and removing even a final product, and its hardened material.

[0006]

[Means for Solving the Problem] this invention person etc. came to complete a header and this invention for it being that to which the resin constituent which has a specific presentation solves those technical problems wholeheartedly as a result of examination, in order to attain the above-mentioned purpose. That is, this invention is the following formula (1) to the carboxyl group in (1) polymer containing at least one carboxyl group (a).

[0007]

[Formula 3]

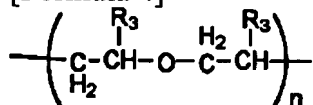


(1)

[0008] (The alkylene whose R1 is a hydrogen atom or a methyl group among a formula and whose R2 is the integer of carbon numbers 2-4, a cyclohexane -1, 4-dimethylene, or the following type (2))

[0009]

[Formula 4]



(2)

[0010] the joining chain shown by (R3 is a hydrogen atom, a methyl group, or an ethyl group here, and n is the number of 1-5) -- it is -- the resin constituent characterized by containing the compound (A) and diluent (B) to which the compound (b) expressed was made to add -- (2) The resin constituent whose compound (b) expressed with a formula (1) is 4-glycidyl ether butyl acrylate, (3) (1) whose weight average molecular weight of a compound (A) is 5000-100,000, or a resin constituent given in (2), (4) (1) whose acid numbers (mgKOH/g) of a compound (A) are 50-150 thru/or the resin constituent of (3) given in any 1 term, (5) It is related with the hardened material of the resin constituent of (1) which is an object for permanent resists thru/or the resin constituent of (4) given in any 1 term, (6), (1), or (5) given in any 1 term.

[0011] The resin constituent of this invention is characterized by containing a compound (A) and a diluent (B). Among the constituent of this invention, 20 - 80 % of the weight is desirable especially desirable, and the (A) component of each component (A) of the resin constituent of this invention and the operating rate of (B) is 30 - 70 % of the weight. (B) Among the constituent of this invention, 20 - 80 % of the weight is desirable especially desirable, and a component is 30 - 70 % of the weight.

[0012] A compound (A) makes the compound (b) expressed with the above-mentioned formula (1) to the carboxyl group in the polymer (a) containing at least one carboxyl group add. The carboxyl group which made polybasic acid anhydrides react to the acrylic resin, the maleic-anhydride copolymer, or the epoxy (meta) acrylate which contains at least one carboxyl group, for example as a polymer (a) containing at least one carboxyl group can be mentioned for content epoxy (meta) acrylate etc. Also in these, the acrylic resin containing at least one carboxyl group is desirable.

[0013] The copolymer to which copolymerization of one sort or two sorts or more of monomers chosen

as an acrylic ethylene nature partial saturation acid from acrylic ester (meta), a vinyl aromatic compound, and an amide system unsaturated compound, for example was carried out as acrylic resin can be used. As an acrylic ethylene nature partial saturation acid, an acrylic acid, 2-carboxyethyl (meta) acrylate, 2-carboxypropyl (meta) acrylate, etc. are raised, for example (meta). (Meta) As acrylic ester, methyl (meta) acrylate, ethyl (meta) acrylate, propyl (meta) acrylate, butyl (meta) acrylate, pentyl (meta) acrylate, hexyl (meta) acrylate, 2-ethylhexyl (meta) acrylate, stearyl (meta) acrylate, methoxy diethylene-glycol (meta) acrylate, ethoxy diethylene-glycol (meta) acrylate, hydroxyethyl (meta) acrylate, hydroxypropyl (meta) acrylate, etc. are raised, for example. As a vinyl aromatic compound, styrene, alpha methyl styrene, vinyltoluene, p-chloro styrene, etc. are raised, for example. As an amide system unsaturated compound, metaacrylamide, diacetone acrylamide, N-butoxy methylacrylamide, acryloyl morpholine, etc. are raised, for example.

[0014] A compound (b) is an acrylate compound which has the glycidyl ether radical expressed with the above-mentioned formula (1). In a formula (1), R1 is a hydrogen atom or a methyl group, and R2 is a joining chain shown by the alkylene which is the integer of carbon numbers 2-4, the cyclohexane -1, 4-dimethylene, or the above-mentioned formula (2). Desirable R2 is the alkylene of a carbon number or a cyclohexane -1, and 4-dimethylene. As alkylene which is the integer of carbon numbers 2-4, the polymethylene of the carbon numbers 2-4, such as dimethylene, trimethylene, and tetramethylen, is mentioned, for example. Moreover, in the joining chain shown by the above-mentioned formula (2), R3 is a hydrogen atom, a methyl group, or an ethyl group, and n is the number of 1-5. Desirable R3 is a hydrogen atom or a methyl group, and n is 2.

[0015] Next, as a compound (b) expressed with a formula (1), 2-glycidyloxy ethyl (meta) acrylate, 2-glycidyloxy propyl (meta) acrylate, 4-glycidyloxy butyl (meta) acrylate, glycidyloxy diethylene-glycol (meta) acrylate, glycidyloxy dipropylene glycol (meta) acrylate, 1, and 4-cyclohexane dimethanol monoglycidyl ether (meta) acrylate etc. can be mentioned, for example. As a desirable thing, 4-glycidyloxy butyl acrylate etc. can be mentioned as 4-glycidyloxy butyl acrylate, 1, 4-cyclohexane dimethanol monoglycidyl ether acrylate, especially a desirable thing.

[0016] To the carboxyl group of said polymer (a), epoxy ring breakage addition of the compound (A) used by this invention can be carried out, and it can obtain the compound (b) expressed with said general formula (1). It is desirable especially desirable to use it in 0.1-0.4 mols to the carboxyl group of a polymer (a) and 1Eq, and the amount of addition of the compound (b) of a general formula (1) is 0.1-0.3 mols. 60-150 degrees C of reaction temperature are desirable, and 10 - 40 hours of reaction time are desirable.

[0017] A catalyst is usually used for epoxy ring breakage addition. As a catalyst to be used, phosphine system compounds, such as quarternary ammonium salt, such as tertiary amine, such as dimethyl benzylamine, triethylamine, tetramethylethylenediamine, and a tree n-octyl amine, tetramethyl ammoniumchloride, a tetramethylammonium star's picture, and a tetrabutylammonium star's picture, and triphenyl phosphine, etc. can be mentioned, for example.

[0018] It is desirable to use a solvent for a reaction. There is especially no limit as a solvent which can be used. For example, aromatic hydrocarbon, such as toluene and a xylene Alcohols, such as a methanol, ethanol, and 2-propanol, an acetone, Ketones, such as a methyl ethyl ketone and methyl isobutyl ketone, diethylether, Ether, such as dibutyl ether and dioxane, ethyl acetate, isobutyl acetate, Ethylene glycol mono-acetate, propylene glycol mono-acetate, Ester, such as dipropylene glycol mono-acetate, and ethylene glycol monoalkyl ether Diethylene-glycol monoalkyl ether and propylene glycol monoalkyl ether Butylene-glycol monoalkyl ether and ethylene glycol dialkyl ether Diethylene-glycol dialkyl ether, such as diethylene-glycol wood ether and diethylene-glycol diethylether, diethylene-glycol monoalkyl ether acetate, solvent naphtha, etc. are raised. These are independent, or may mix and use two or more sorts.

[0019] 5,000-100,000 are desirable, and are 10,000-70,000 more preferably, and the weight average molecular weight of a compound (A) is 20,000-50,000 especially preferably, when the solubility to the organic solvent or monomer as a diluent, workability, and the thermal resistance of a hardened material are taken into consideration. Moreover, it is desirable especially desirable that it is 50 - 150 mgKOH/g,

and the acid number of a compound (A) is 50 - 120 mgKOH/g. If less than 50 mgKOH/g, the removal nature for a non-hard spot after the resist formation by the dilute-alkali water solution will worsen, and when 150 mgKOH/g is exceeded on the other hand, there is an inclination for the electrical property of a hardening coat and a humidification property to worsen.

[0020] A diluent (B) is used in this invention. As a diluent (B), organic solvents (B-1) and reactant monomers (B-2) can be mentioned, for example. As organic solvents (B-1), petroleum solvents, such as ester, such as glycol ether, such as aromatic hydrocarbon, such as ketones, such as ethyl methyl ketone and a cyclohexanone, toluene, a xylene, and tetramethyl benzene, dipropylene glycol wood ether, and dipropylene glycol diethylether, ethyl acetate, butyl acetate, butyl-cellosolve acetate, carbitol acetate, and propylene-glycol-monomethyl-ether acetate, the petroleum ether, petroleum naphtha, hydrogenation petroleum naphtha, and solvent naphtha, etc. are raised, for example. As reactant monomers (B-2), carbitol (meta) acrylate, phenoxy ethyl (meta) acrylate, TORIMECHI roll pro pantry (meta) acrylate, pentaerythritol tetrapod (meta) acrylate, tris (hydroxyethyl) iso SHIANURETOTORI (meta) acrylate, dipentaerythritol hexa, PENTA (meta) acrylate, etc. are raised, for example. These diluents (B) are used as independent or two or more sorts of mixture. Moreover, a diluent (B) may be added at the time of the epoxy (meta) acrylate (resin A) composition.

[0021] It is desirable to use a photopolymerization initiator (C) and a hardening component (D) for the resin constituent of this invention in addition to (A) and the (B) component. Among the constituent of this invention, 1 - 20 % of the weight is desirable especially desirable, and the operating rate of a photopolymerization initiator (C) is 1 - 10 % of the weight. Moreover, the amount of the hardening component (D) which is used as two or more sorts of mixture, and is contained in the constituent of this invention has the inside of a constituent, and 0 - 50 desirable especially desirable independently % of the weight, and a hardening component (D) is 3 - 40 % of the weight. The purpose of using a hardening component (D) raises many properties as resists, such as adhesion, thermal resistance, and plating-proof nature.

[0022] As a photopolymerization initiator (C), for example A benzoin, benzoin methyl ether, Benzoin, such as benzoin iso-propyl ether, an acetophenone, A 2 and 2-dimethoxy-2-phenyl acetophenone, 2, and 2-diethoxy-2-phenyl acetophenone, 1 and 1-dichloro acetophenone, 1-hydroxy cyclohexyl phenyl ketone, 2-methyl-1-[4-(methylthio) phenyl]-2-morpholinopropane-1-ON, Acetophenones, such as N and N-dimethylamino acetophenone, 2-methyl anthraquinone, 2-ethyl anthraquinone, 2-tert-butyl anthraquinone, Anthraquinone, such as 1-chloro anthraquinone and 2-amyl anthraquinone Thioxan tons, such as 2, 4-diethylthio xanthone, 2-chloro thioxan ton, and 2-isopropyl thioxan ton Ketals, such as benzyl dimethyl ketal and acetophenone dimethyl ketal A benzophenone, methyl benzophenone, 4, and 4'-dichloro benzophenone, A 4 and 4'-screw diethylamino benzophenone, a MIHIRAZU ketone, There is benzophenones [, such as 4-benzoyl-4'-methyl diphenyl sulfide, ], 2 and 4, and 6-trimethyl benzoyl diphenylphosphine oxide etc., and it can use combining independent or two sorts or more.

[0023] Furthermore, a photosensitizer like the third class amines, such as N and N-dimethylamino ethyl benzoate ester, N, and N-dimethylamino isoamyl benzoate ester, pentyl-4-dimethylamino benzoate, triethylamine, and triethanolamine, can be used for a photopolymerization initiator (C) combining independent or two sorts or more.

[0024] It may react by a hydroxyl group, a carboxyl group, etc. heat, ultraviolet rays, etc. of what does not have a partial saturation double bond, for example, and itself hardens by heat, ultraviolet rays, etc. as a hardening component (D), and the (A) component used by this invention. Specifically, the bisphenol A system compounds, such as urea compounds, such as melamine derivatives, such as an epoxy compound which has one or more epoxy groups, a hexamethoxy melamine, a hexa butoxy-ized melamine, and a condensation hexamethoxy melamine, and a dimethylolurea, and tetra-methylol bisphenol A, an oxazoline compound, etc. are raised into 1 molecule.

[0025] As an epoxy compound which has one or more epoxy groups in 1 molecule For example, NOHORAKKU mold epoxy resins, such as a bisphenol mold epoxy resin, EPPN-201, EOCN-103, EOCN-1020, and BREN (all are the Nippon Kayaku Co., Ltd. make), The novolak mold epoxy resin of bisphenol A, such as Epiclone N-880 (Dainippon Ink & Chemicals, Inc. make), Amino-group content

epoxy resins, such as YL-931 and YL-933 (all are the products made from oil-ized Shell Epoxy), Rubber modified epoxy resins, such as Epiclon TSR-601 (Dainippon Ink & Chemicals, Inc. make) and R-1415-1 (product made from A C R), Triglycidyl isocyanates, such as TEPIC (product made from Nissan Chemistry), BIKISHIRE Norian mold epoxy resins, such as YX-4000 (product made from oil-ized Shell Epoxy), Here where cycloaliphatic epoxy resin, such as mixture of the bisphenol mold epoxy resin of YL-612H grade and a BIKISHIRE Norian mold epoxy resin and the SEROKI side 2021 (Daicel Chemical Industries, Ltd. make), etc. is mentioned is made.

[0026] As a bis-FENORU mold epoxy resin, for example Epicoat 1009 and 1031 (all are the products made from oil-ized Shell Epoxy), Epiclon N-3050, N-7050 (all are the Dainippon Ink & Chemicals, Inc. make), The bisphenol A mold epoxy resins, such as DER-642U and DER-673MF (all are the Dow Chemical Co. make), Hydrogenation bisphenol A mold epoxy resins, such as ST-2004 and ST-2007 (all are the Tohto Kasei Co., Ltd. make), Bisphenol female mold epoxy resins, such as YDF-2004 and YDF-2007 (all are the Tohto Kasei Co., Ltd. make), SR-BBS, SR-TBA-400 (all are the products made from Sakamoto Pharmaceutical industry), Bisphenol smooth S form epoxy resins, such as YDB-600, the bromination bisphenol A mold epoxy resin of YDB-715 grade (all are the Tohto Kasei Co., Ltd. make), and Epiclon EXA-1514 (Dainippon Ink & Chemicals, Inc. make), etc. are raised.

[0027] When using an epoxy compound in the above and a hardening component (D), in order to raise properties, such as adhesion, chemical resistance, and thermal resistance, further, it is desirable to use together an epoxy resin hardening (promotion) agent. As an epoxy resin hardening (promotion) agent, an imidazole derivative, guanamines, polyamine, the amine complex of a boron trifluoride, triazine derivatives, the third class amines, polyphenol, organic phosphines, an optical cationic polymerization catalyst, etc. are mentioned, for example. these epoxy resin hardening (promotion) agents are independent -- or two or more sorts are mixed and it uses. To said epoxy compound 100 weight section, 0.01 - 25 weight section is desirable especially desirable, and the amount used is 0.1 - 15 weight section.

[0028] As an imidazole derivative used as an epoxy resin hardening (promotion) agent For example, 2MZ(s), 2E4MZ, C11Z, C17Z, 2PN, 1 B-2 MZ, 2 MZ-CN, 2E4 MZ-CN, C11 Z-CN, 2 PZ-CN, 2 PHZ-CN, 2 MZ-CNS, 2E4 MZ-CNS, 2 PZ-CNS, 2 MZ-AZ1NE, 2E4 MZ-AZ1NE, C11 Z-AZ1NE, 2 MA-OK, 2P4MHZ, 2PHZ, a 2P4BHZ grade (all are the Shikoku Chemicals Corp. make), etc. are mentioned, and acetoguanamine, benzoguanamine, etc. are mentioned as guanamines, for example. As polyamine, diamino diphenylmethane, m-phenylenediamine, meta xylene diamine, diaminodiphenyl sulfone, a dicyandiamide, a urea, a melamine, multi-base hydrazide, etc. are mentioned, for example, and ethyl diamino-S-triazine, 2, 4-diamino-S-triazine, 2, and 4-diamino-6-xylyl-S-triazine etc. is mentioned as triazine derivatives, for example.

[0029] As the third class amines used as an epoxy resin hardening (promotion) agent For example, trimethylamine, triethanolamine, N, and N-dimethyl octyl amine, N-benzyl dimethylamine, a pyridine, N-methyl morpholine, a hexa (N-methyl) melamine, 2, 4, 6-tris (dimethylamino phenol), tetramethyl guanidine, m-aminophenol, etc. are mentioned. As polyphenol For example, a polyvinyl phenol, a polyvinyl phenol bromination object, a phenol novolak, an alkylphenol novolak, etc. are mentioned. As organic phosphines, tributyl phosphine, triphenyl phosphine, a tris-2-cyano ethyl phosphine, etc. are mentioned, for example, and diphenyliodonium hexafluoroantimonate, diphenyliodonium tetrakis perfluoro FENIRUBORETO, triphenylsulfonium hexafluorophosphate, Optomer SP-170 (Asahi Denka Kogyo K.K. make), etc. are mentioned as an optical cationic polymerization catalyst, for example.

[0030] Further, inorganic bulking agents, such as barium-sulfate, barium titanate, silicon oxide powder, and fines-like silicon oxide, an amorphism silica, talc, clay, a magnesium carbonate, a calcium carbonate, an aluminum oxide, an aluminum hydroxide, and mica powder, can be used for the constituent of this invention if needed in order to improve properties, such as adhesion and a degree of hardness. 0 - 60 % of the weight in the constituent of this invention is desirable especially desirable, and the amount used is 0 - 40 % of the weight.

[0031] The need is accepted. Furthermore, a copper phthalocyanine blue, Phthalocyanine Green, an eye -- a man past his prime - Green, Diarylide Yellow, and a crystal violet -- Coloring agents, such as

titanium oxide, carbon black, and Naphthalene Black, hydroquinone, Polymerization inhibitor, such as the hydroquinone monomethyl ether and phenothiazin, Thickeners, such as asbestos, Orr Ben, Benton, and a montmorillonite, a silicone system, Various kinds of additives like adhesion grant agents, such as defoaming agents, such as a fluorine system and a giant-molecule system, and/or a leveling agent, an imidazole system adhesion grant agent, a thiazole system adhesion grant agent, a triazole system adhesion grant agent, and a silane coupling agent, can be used. When using these additives etc., the amount used may be suitably fluctuated among the constituent of this invention according to the purpose of use, respectively, although about 0.5 - 30 % of the weight is a temporary standard. Moreover, binder resin, such as copolymers of ethylene nature unsaturated compounds, such as acrylic ester, polyether sulphone resin, and polyester resin, etc. can be used.

[0032] If needed, the resin constituent of this invention can blend (A) and the (B) component at a desirable aforementioned rate, and can prepare (C), the (D) component, an inorganic bulking agent, and other additives for them by mixing, the dissolution, distribution, etc. to homogeneity by a roll mill etc. again.

[0033] The resin constituent of this invention is used that it is liquefied as an object for permanent resists, and preferably. It applies by the thickness of 20-60 micrometers on a printed wired board. 60-100 degrees C, Heat-treat and remove a solvent, and lay on it a 10 - 60-minute about room, and the mask which has a predetermined pattern, and ultraviolet rays are irradiated. A part for an unexposed part is developed with a developer, a pattern is formed, ultraviolet rays are irradiated further after that if needed, and the permanent protective coat with which are satisfied of many properties is obtained by subsequently heat-treating at 100-200 degrees C. As a developer, alkali water solutions, such as a sodium carbonate, a sodium hydroxide, and a potassium hydroxide, etc. can be used, for example.

[0034] drying the resin constituent of this invention with the drying furnace set as 60-100 degrees C after using a roll coater, a doctor bar, a wire bar method, the tipping method, the spin coat method, the gravure method, the doctor blade method, etc. and applying this constituent on a base film (mold releasing film), and removing the solvent of the specified quantity -- moreover, it can consider as a dry film by sticking a mold releasing film etc. if needed. Under the present circumstances, the thickness of the resin constituent (resist) of this invention on a base film is prepared by 15-150 micrometers. As the above-mentioned base film, films, such as polyethylene terephthalate and polypropylene, are used suitably, for example. What is necessary is to strip a mold releasing film, to imprint to a substrate, and just to carry out exposure, development, and heat-treatment like the above, in order to use this dry film.

[0035] The hardened material of the resin constituent of this invention obtained by the above-mentioned approach is used for the electrical and electric equipment and electronic parts like the printed wired board which has SURUHOU as a permanent resist. Moreover, the thickness of the hardened material layer of a printed wired board which has the hardened material layer of the resin constituent of this invention has desirable about 20-60 micrometers.

[0036]

[Example] Hereafter, an example explains this invention still more concretely.

The synthetic example 1 (synthetic example of a compound (A))

Dipropylene-glycol-monomethyl-ether 200g and 13.1g of t-butylperoxy2-ethylhexanoate were introduced, and it was dropped at them after the temperature up, having applied [ 172.2g / of methacrylic acids /, methyl methacrylateg / 154.5 / and 2, and 2'-azobis (2-methyl butyronitrile) 10.5g and dipropylene-glycol-monomethyl-ether 126g ] it to 95 degrees C for 3 hours. The trunk polymer which ripens after dropping for 4 hours and has a carboxyl group was compounded. Next, 4-glycidyoxy butyl acrylate 119.3g and triphenyl phosphine 2.9g, and methyl hydroquinone 0.5g were added to the above-mentioned trunk polymer solution, and it was made to react to it at 100 degrees C for 10 hours. Let the obtained polymer be a compound (A-1). The acid number (solid content) of a compound (A-1) was [ 792.7 and the weight average molecular weight of 165 mgKOH/g and the double bond equivalent (the amount of gram-weights of the resin per one mol of partial saturation radicals) ] 15,000.

[0037] The synthetic example 2 (synthetic example for the example of a comparison)

a cresol novolak mold epoxy resin (the Nippon Kayaku Co., Ltd. make and EOCN-104S --) Weight-per-



epoxy-equivalent 210 220g, 72g [ of acrylic acids ], and methyl hydroquinone 0.2g and carbitol acetate 158g are taught. Heat and dissolve in 80 degrees C, subsequently to 60 degrees C cool, and triphenyl phosphine 1.3g is taught. It heated at 98 degrees C and the reaction was performed for about 32 hours, next 109g [ of tetrahydro phthalic anhydride ] and carbitol acetate 58.7g was taught, the reaction was performed at 95 degrees C for 10 hours, and the reactant was obtained. The acid number (solid content) of a reactant was 100 mgKOH/g.

[0038] Examples 1 and 2 According to the combination presentation (a numeric value is the weight section.) shown in example of comparison 1 table 1, each component was mixed, it distributed and kneaded, and the resin constituent of this invention was obtained. The obtained resin constituent was applied by the thickness of 30 micrometers on the laminate, it dried for 60 minutes at 80 degrees C, and the resist which consists of a resin constituent of this invention was produced. Subsequently, the negative mask was contacted on this resist and ultraviolet rays were irradiated using the ultrahigh pressure mercury lamp. It is a part for an unexposed part with 1.5% sodium-carbonate water solution For 60 seconds and 2.0kg/cm<sup>2</sup> Negatives were developed with spray pressure. Heat-treatment was performed for ultraviolet rays on the whole surface for 30 minutes at an exposure and 150 degrees C after rinsing desiccation. This was immersed in non-electrolytic copper plating liquid at 70 degrees C for 10 hours, about 20-micrometer non-electrolytic copper plating coat was formed, and the additive process multilayer printed wiring board was produced. Thus, the result evaluated by the process in which an additive process multilayer printed wiring board is obtained, about the property of a resist is shown in Table 1.

[0039] The evaluation approach (development nature)

O .... At the time of development, ink was removed completely and perfect development was made.

x .... At the time of development, residue remains and there is a part which is not developed.

(Solvent resistance) The resist hardening film was immersed in the acetone for 20 minutes, and the condition was viewed.

O .... It was completely changeless.

x .... Blistering and HAKURI occurred.

(Plating-proof acidity or alkalinity)

O .... Change is not seen at all at a radio solution coppering process.

\*\* .... Discoloration is seen a little at a radio solution coppering process.

x .... Discoloration, blistering, and HAKURI occurred at the radio solution coppering process.

[0040] (Solder thermal resistance) JIS C According to the test method of 6481, 10-second immersion of the test piece to a solder bath was performed 3 times at 260 degrees C, and change of an appearance was evaluated.

O .... With no appearance change.

\*\* .... Discoloration of the hardening film is accepted.

x .... The float of the hardening film, peeling, those with solder diving.

Used postflux (rosin system): (Note) JIS C The flux according to 6481 is used.

[0041] (Flux resistance for levelers) Immersion was performed 3 times for 10 seconds, and change of an appearance was evaluated after 10-minute immersion in boiling water.

O .... With no appearance change.

\*\* .... Discoloration of the hardening film is accepted.

x .... The float of the hardening film, peeling, those with solder diving.

Used flux for levelers: (Note) Product made from MEKKU, W-121 [0042]

[Table 1]

Table 1 Combination presentation and characteristic test combination presentation An example The example of a comparison 1 2 The compound obtained in the example 1 of 1 composition (A) 169 The reactant obtained in the example 2 of 169 composition 154 propylene-glycol-monomethyl-ether acetate 25KAYARAD(s) DPHA \*1 5 5 5EOCN-104S \*2 20 7.5 7.5 benzyl dimethyl ketal 33 3 Aerosil 380 \*3 3 3 32, 4-diethylthio xanthone 0.5 0.5 0.5 melamines (epoxy curing agent) 3 2 Two dicyandiamides (epoxy curing agent) 2 1 1 diacid-ized silica 35 35 35 ----- Development nature

O O O Plating-proof liquid O O x solvent resistance O O O solder thermal resistance Postflux resistance  
O O O Flux resistance for levelers O O O [0043] Note \*1 KAYARAD DPHA: The Nippon Kayaku Co.,  
Ltd. make, dipentaerythritol PENTA, and hexa acrylate mixture.

\*2 EOCN-104S : the Nippon Kayaku Co., Ltd. make, a cresol novolak mold epoxy resin, weight per  
epoxy equivalent 220, 92 degrees C of softening temperatures.

\*3 Aerosil 380 : the product made from Japanese Aerosil, an anhydrous silica.

[0044] The resin constituent of this invention has good development nature, and the hardened material is  
excellent in solvent resistance, plating-proof nature, and solder thermal resistance so that clearly from  
the evaluation result of Table 1.

[0045]

[Effect of the Invention] The resin constituent of this invention and its hardened material are excellent in  
the plating-proof acidity or alkalinity over the electroless deposition performed under solvent resistance,  
an elevated temperature, and high alkaline conditions for a long time although development is easy with  
high resolution, also offer the thermal resistance which also bears the temperature around 260 degrees C  
of a soldering process further, and fit especially manufacture of a printed wired board as a permanent  
resist.

---

[Translation done.]